

CLAIMS:

1. An aqueous acidic solution for forming a conversion coating on the surface of a metallic material, said solution containing at least one rare earth element (as herein defined) containing species, an accelerator additive selected from the group consisting of metals of Groups IB, IIB, IVA, VA, VIA and VIII of the Periodic Table, a peroxidic species and at least one acid selected from the group of mineral acids, carboxylic acids, sulphonic acids and phosphonic acids, wherein said solution contains no more than 20 mg/litre each of fluoride and of phosphate, and the solution is substantially free of chromate.
2. The solution of claim 1, further including a total chloride concentration within the range of from 30 to 1500 mg/litre, preferably from 50 to 1500 mg/litre.
3. The solution of claim 1, wherein the accelerator additive is selected from the elements Cu, Ag, Au, Cd, Hg, Ni, Pd, Pt, Co, Rh, Ir, Os, Sn, Pb, Sb, Bi, Se, and Te, preferably selected from Cu, Ag, Sn, Pb, Sb, Bi, Se and Te.
4. The solution of claim 1, wherein the solution contains only one accelerator additive.
5. The solution of claim 1, wherein the accelerator additive is Cu, preferably at a concentration from 0.01 to 5 mmol/litre.
6. The solution of claim 1, wherein the at least one acid is selected from the group comprising sulphuric acid, sulphamic acid, hydrochloric acid, nitric acid, perchloric acid, carboxylic acids, alkyl sulphonic acids, aryl sulphonic acids, alkyl phosphonic acids and aryl phosphonic acids.
7. The solution of claim 1, wherein said at least one rare earth element containing species comprises ions and/or complex species of a mixture of REE wherein the ratio of cerium to total REE is at least 5% by weight, preferably at least 30% by weight, more preferably at least 60% by weight.

8. The solution of claim 1, wherein the concentration of rare earth element containing species is in the range of 0.5 to 1000 g/l, preferably from 1 to 60 g/l, more preferably from 2 to 30 g/l.
- 5 9. The solution of claim 1, wherein the rare earth elements are introduced into the coating solution in the form of a soluble salt selected from cerium (III) containing chloride, cerium (III) containing sulphate, cerium (III) containing sulphamate, cerium (III) containing nitrate, cerium (III) containing perchlorate and cerium (III) containing methanesulphonate, preferably said soluble salt is
- 10 formed by reaction of cerium carbonate with an appropriate acid.
10. The solution of claim 1, wherein said rare earth element is cerium, present at a concentration in the range from 0.01 to 0.5 mol/litre.
- 15 11. The solution of claim 1, wherein said peroxidic compound is selected from the group of peroxy acids, peroxy salts and peroxy compounds, and is preferably hydrogen peroxide.
12. The solution of claim 1, wherein the amount of the peroxidic compound,
- 20 calculated as equivalent amount of hydrogen peroxide, is in the range from 1 to 200 g/l, preferably 1 to 100 g/l, more preferably 2 to 50 g/l, more preferably 3.4 to 34 g/l.
13. The solution of claim 1, wherein the concentration of at least one said
- 25 accelerator additive is in the range from 0.0001 to 1.2 g/l, preferably from 0.001 to 1 g/l, more preferably from 0.005 to 0.1 g/l, more preferably from 0.01 to 0.06 g/l.
14. The solution of claim 1, wherein the total concentration of the accelerator
- 30 additive is from 0.0001 to 0.15 g/l.
15. The solution of claim 1, wherein the accelerator additive is in a concentration range from 0.01 to 5 mmol/litre, preferably from 0.02 to 5 mmol/litre.

16. The solution of claim 1, wherein the accelerator additive is present in solution as a complexed species, wherein the complexing agent is preferably an amino carboxylic acid, such as glycine, alanine and/or glycine ethyl ester, ethylenediaminetetraacetic acid (EDTA), nitriloacetic acid (NTA),
5 hydroxyethylenediaminetriacetic acid (HEDTA) and/or corresponding salts thereof, more preferably glycine.
17. The solution of claim 1, wherein the accelerator additive is present in solution as an uncomplexed species.
- 10 18. The solution of claim 1 having a pH value from 1.0 to 2.9, preferably from 1.7 to 2.5, more preferably from 1.9 to 2.2.
19. The solution of claim 1, wherein the metallic material is aluminium or
15 aluminium alloy and the solution contains not more than 500 mg/l nitrate content, preferably not more than 300 mg/l, more preferably not more than 200 mg/l, particularly preferred not more than 50 mg/l.
20. The solution of claim 1, wherein the rare earth element is cerium, said
20 accelerator additive is copper and said peroxidic species is a peroxidic compound, said solution further containing sulphate and/or sulphamate species and at least 50 mg/l of chloride.
21. The solution of claim 1, wherein said rare earth element is cerium and
25 said peroxidic species is hydrogen peroxide.
22. A process for forming a conversion coating on the surface of a metallic material including at least one step of contacting said surface with an aqueous acidic solution according to claim 1.
- 30 23. The process of claim 22, wherein said at least one contacting step is preceded by at least one of the steps of cleaning, pickling, rinsing and deoxidation with an acidic solution.

24. The process of claim 22, further including at least one rinsing step after said contacting step.

25. The process of claim 22, wherein said contacting step comprises
5 immersing, spraying, rolling on or swabbing said surface with said solution.

26. The process of claim 22, wherein a lubricant, a sealant and/or a paint is applied onto the conversion coating.

10 27. The process of claim 22, wherein said metallic material is an aluminium, an aluminium alloy, magnesium, magnesium alloy, zinc, or a zinc alloy, preferably an aluminium alloy of the series 3000, 5000 or 6000.

15 28. The process of claim 22, wherein said contacting step is conducted at a temperature of solution of less than 65°C, preferably greater than 18°C, more preferably greater than 35°C and less than 50°C.

19 29. A surface treated part of a metallic material having a conversion coating thereon resulting from treatment with an aqueous acidic solution according to
20 claim 1.

25 30. The surface treated part of a metallic material of claim 29, wherein said metallic material is aluminium, aluminium alloy, magnesium, magnesium alloy, zinc, or a zinc alloy, preferably an aluminium alloy of the series 3000, 5000 or 6000.

31. The surface treated part of a metallic material of claim 29, wherein said conversion coating contains at least 5% by weight of rare earth elements, preferably in the range of 20 to 92% by weight, more preferably in the range
30 from 50 to 88% by weight, particularly preferably from 60 to 85% by weight.

32. The surface treated part of a metallic material of claim 29, wherein the weight of said conversion coating is from 0.01 to 100 g/m², preferably from 0.05 to 5 g/m², more preferably from 0.1 to 3 g/m², if used as a substrate for

subsequent painting, or from 0.4 to 10 g/m², if not used as a substrate for subsequent painting.

33. A liquid acidic aqueous concentrate for the make-up of an aqueous acidic solution according to claim 1, wherein said concentrate includes at least 80 g/litre, preferably at least 100g/litre, more preferably at least 125 g/litre, of total rare earth element (as herein defined) containing species, and at least one acid selected from the group of mineral acids, carboxylic acids, sulphonic acids and phosphonic acids, wherein the concentrate contains no more than 100 mg/l each of fluoride and of phosphate and the concentrate contains substantially no chromate.

34. The concentrate of claim 33, further including an accelerator additive selected from the group consisting of metals of Groups IB, IIB, IVA, VA, VIA and VIII of the Periodic Table, preferably selected from the group of Cu, Ag, Au, Cd, Hg, Ni, Pd, Pt, Co, Rh, Ir, Ru, Os, Sn, Pb, Sb, Bi, Se and Te, more preferably selected from the group of Cu, Ag, Sn, Pb, Sb, Bi, Se and Te, most preferably Cu.

35. The concentrate of claim 33, wherein said rare earth element is cerium.

36. The concentrate of claim 33, wherein said acid is selected from the group comprising nitric acid, perchloric acid, sulphuric acid, methanesulphonic acid and sulphamic acid.

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37. A liquid acidic aqueous concentrate for the replenishing of an aqueous acidic solution according to claim 1, said concentrate containing rare earth ions and monovalent anions in a molar ratio of total rare earth ions : monovalent anions of from 1 : 200 to 1 : 6.

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38. A liquid acidic aqueous concentrate for the replenishing of an aqueous acidic solution according to claim 1, said concentrate containing rare earth ions and divalent anions in a molar ratio of total rare earth ions : divalent anions from 1 : 100 to 1 : 3.

39. A liquid acidic aqueous concentrate for the replenishing of an aqueous acidic solution according to claim 1, said concentrate containing at least one metal selected from Groups IB, IIB, IVA, VA, VIA and VIII, preferably from the group of Cu, Ag, Au, Cd, Hg, Ni, Pd, Pt, Co, Rh, Ir, Ru, Os, Sn, Pb, Sb, Bi, Se and Te and anions such that the molar ratio of the sum of the elements in this group : anions is in the range from 1 : 50 to 1 : 10,000.

40. The concentrate of claim 37, further including at least one peroxidic compound.

41. The surface treated part of claim 29, wherein said part is used in a process of cold forming, glueing, welding and/or other forms of joining.

42. The surface treated part of claim 29, wherein said part is a coil.

43. The process of claim 22, wherein said metallic material comprises a coil and the conversion coated coil is preferably treated before or after coating with another corrosion inhibiting solution, such as a passivation treatment, a primer or a paint.